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(54) **Water based dispersions of percarboxylic acids**

Wässrige Dispersionen von Percarbonsäure

Dispersions aqueuses d'acides percarboxyliques

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Description

[0001] The present invention relates to water dispersions of percarboxylic acids in crystalline form usable in detergent and/or hygienizing, cosmetic systems. More specifically water dispersions of crystals of ϵ -phthalimido peroxyhexanoic acid, herein called PAP, having a high chemical stability and an improved physical stability, usable in detergent and hygienizing systems stable during the time for at least 6 months.

[0002] Organic peroxyacids are well known for their efficacy as bleaching and hygienizing agents also at low temperatures. To this class of compounds belong peroxycarboxylic acids solid at room temperature usable in formulations in powder or in tablets typical of the detergency.

[0003] Among peroxycarboxylic acids of particular interest the ϵ -phthalimido peroxyhexanoic acid is very effective as a bleaching, hygienizing and deodorizing agent, and in general as oxidizer, already under mild conditions of temperature and pH. The ϵ -phthalimido peroxyhexanoic acid is suitable for the preparation of formulations for use in the detergent and cosmetic industry, since it has an exceptional thermal and storage stability as well as a particularly favourable toxicological and ecotoxicological profile.

[0004] It is besides well known for the applications in the detergency and hygienizing field to use liquid systems having an aqueous base containing active principles not dangerous either for men or for the environment, having a sufficient chemical and physical stability such as to be used in consumer goods, for the distribution and exposure to the public for even long periods of time. For these systems an high chemical stability and an improved physical stability are required, in environmental temperature conditions from 15°C to 35°C for at least 6 months.

[0005] In the case of organic peroxyacids to be used as active principles for said liquid systems in the detergency and hygienizing field, it is difficult to formulate water-based systems with the above mentioned chemical and physical stability properties.

[0006] In particular in the case of solid peroxyacids as the mentioned ϵ -phthalimido peroxyhexanoic acid, the formulations having a water base are heterogeneous systems, wherein the peracid crystals are dispersed in a continuous water phase.

[0007] It is known from the technology of the production of the ϵ -phthalimido peroxyhexanoic acid to obtain dispersions of crystals of said acid in water mediums (slurry), characterized by a satisfactory chemical stability of the acid itself but by a low physical stability: in fact said slurries show, in absence of stirring, segregation and sedimentation also in short times. This means that these industrially useful products are difficult to be used as consumer goods due to their insufficient physical stability, since as known, for this application the products must be stable upon storage without stirring for at least 6 months.

[0008] It is known from the prior art to use chemical auxiliary agents having properties of thickening and viscosity improver agents to be introduced in the water-based crystal dispersions to improve the physical stability thereof. But even though numerous auxiliary compounds are known, able to stabilize water-based dispersions of crystals of chemical compounds having relatively low reactivity, in the case of the ϵ -phthalimido peroxyhexanoic acid, its high chemical reactivity makes it impossible to produce a water-based system having a high chemical stability and improved physical stability lasting during the time.

[0009] US 5,073,285 and US 4,992,194 disclose structured aqueous liquids containing a suspended peroxy bleach and a stabilising agent for the peroxyacid consisting of a polymer with hydrophilic and hydrophobic monomer units, wherein some of the hydrophilic monomer units are provided with hydrophobic functional groups.

[0010] The need was therefore felt to identify auxiliary agents suitable to develop water-based systems containing crystals of ϵ -phthalimido peroxyhexanoic acid in the form of dispersions having a high chemical stability and improved physical stability during the time.

[0011] The Applicant has surprisingly and unexpectedly found auxiliary agents suitable for the preparation of chemically and physically stable water based dispersions of the ϵ -phthalimido peroxyhexanoic acid.

[0012] An object of the present invention are water-based dispersions of the ϵ -phthalimido peroxyhexanoic acid comprising as stabilizers copolymers of methyl-vinyl-ether with the acid and/or the maleic anhydride, in 1:1 ratio having an alternate structure.

[0013] Said copolymers generally have a weight average molecular weight in the range 200,000-2,000,000.

[0014] Such stabilizers are in the market as, e.g., GANTREZ[®] by ISP.

[0015] The amount of PAP can range between 1-30% by weight, preferably between 3-20% by weight.

[0016] The amount of the stabilizers (auxiliary agents) of the invention generally varies in the range 0.2-5% by weight, preferably 1.5-4% by weight, still more preferably 2-4% by weight.

[0017] The organic peroxyacid PAP is well known in the prior art for its use in the detergency and hygienizing field and also for its use in bleach, see EP 325,289.

[0018] The organic peroxyacid PAP contained in the suspensions (dispersions) of the present invention is in the form of crystalline particles having sizes generally in the range of 5-200 micron, as determinable by optical microscope.

[0019] In the water-based dispersions of the ϵ -phthalimido peroxyhexanoic acid of the present invention additional

components such as polymers of natural origin of polysaccharide type, preferably selected from guar rubber and xanthan rubber, products described, for example in Merck Index, edition XII, number 4,602 of page 780 and number 10,191 of page 1,718, respectively, can optionally be present. In the suspension said optional stabilizers are in the range 0.1%-1.5% by weight.

[0020] The total amount of stabilizers contained in the dispersion is in the range 0.2-5% by weight, preferably 1.5-4% by weight, still more preferably 2-4% by weight.

[0021] Other optional components which can be added having the function to stop the catalytic action of heavy metal ions on the decomposition of the peroxyacid, are chelants and/or sequestrants in amounts from 0.005 to 5% by weight. Quinoline and its salts, alkaline metal polyphosphates, picolinic and dipicolinic acid, mono- or polyphosphonic acids, for example preferably the 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) can be mentioned.

[0022] The physical stability in the time, at room temperature, of the dispersions of the present invention (see for example Table 1) can be visually checked by ascertaining the unmixing presence or absence after six months. More suitably it can be checked that in the period of two months no unmixing appears and that the dispersion viscosity, generally in the range of 500-2,000 centipoise, does not change in absolute value more than 10%, preferably 7%, when a copolymer of methylvinylether with maleic acid is used in 1:1 ratio having a weight average molecular weight of 1,900,000. With said viscosity variations, the Applicant has found that the dispersion remains physically stable for at least six months.

[0023] The chemical stability during the time, at room temperature, of the dispersions of the present invention is determined by the active oxygen content, determined by iodometric titration and expressed in %, the 100% being defined as the content of active oxygen at the beginning of the storage.

[0024] The viscosity of the PAP water-based dispersions according to the present invention, expressed in centipoise (cPs), is measured with a Brookfield viscometer at 25°C with rotary probe at 60 rpm.

[0025] The following examples are given for illustrative but not for limitative purposes of the present invention.

EXAMPLE 1

[0026] 25 g of an alternated copolymer methylvinylether-maleic acid, having a molecular weight of 1.9×10^6 , are slowly added to 385 g of distilled water. Stirring is maintained for 20 minutes until complete dissolution of the polymer.

[0027] 170 g of ϵ -phthalimido peroxyhexanoic acid in powder are separately dispersed in 400 g of distilled water.

[0028] The two above described liquids are mixed together and kept under stirring for 20 minutes; a creamy liquid having a Brookfield viscosity of 830 cPs is obtained. The physical and chemical stability data during the time are reported respectively in Tables 1 and 2.

EXAMPLE 2

[0029] 10 g of an alternated copolymer methylvinylether-maleic acid, having a molecular weight of 1.9×10^6 , are slowly added to 385 g of distilled water. Stirring is maintained for 20 minutes until complete dissolution of the polymer.

[0030] 170 g of ϵ -phthalimido peroxyhexanoic acid in powder and 10 g of Guar rubber are separately dispersed in 400 g of distilled water.

[0031] The two above described liquids are mixed together and kept under stirring for 20 minutes; a creamy liquid having a Brookfield viscosity of 980 cPs is obtained. The physical and chemical stability data during the time are reported respectively in Tables 1 and 2.

EXAMPLE 3

[0032] 10 g of an alternated copolymer methylvinylether-maleic acid, having a molecular weight of 1.9×10^6 , are slowly added to 385 g of distilled water. Stirring is maintained for 20 minutes until complete dissolution of the polymer.

[0033] 170 g of ϵ -phthalimido peroxyhexanoic acid in powder and 3 g of Xanthan rubber are separately dispersed in 432 g of distilled water.

[0034] The two above described liquids are mixed together and kept under stirring for 20 minutes; a creamy liquid having a Brookfield viscosity of 910 cPs is obtained. The physical and chemical stability data during the time are reported respectively in Tables 1 and 2.

EXAMPLE 4 comparative (comp)

[0035] 5 g of an acrylic-sodium acrylate-acrylamide acid copolymer, having a molecular weight of 5×10^6 , commercialized as ECOCLAR® by AUSIMONT, are solubilized in 825 g of distilled water.

[0036] A solution at pH 7, having a Brookfield viscosity of 960 cPs is obtained.

[0037] In such solution 170 g of ϵ -phthalimido peroxyhexanoic acid in powder are dispersed under mild stirring; a suspension having a Brookfield viscosity of 1,100 cPs is obtained. The physical and chemical stability data during the time are reported respectively in Tables 1 and 2. The chemical instability of the suspension is evident, wherefore the product has no interest from the application point of view.

EXAMPLE 5 comparative (comp)

[0038] 170 g of ϵ -phthalimido peroxyhexanoic acid in powder are dispersed in 817 g of distilled water. 10 g of Guar rubber and 3 g of Xanthan rubber are added under stirring. The obtained mixture is subjected to stirring for 20 minutes until dissolution of the stabilizers; a suspension having a Brookfield viscosity of 1,100 cPs is obtained. The physical and chemical stability data during the time are reported respectively in Tables 1 and 2.

Table 1

Examples	physical stability in the time at room temperature		
	48 hours	8 weeks	24 weeks
1	not unmixed viscosity 830cPs	not unmixed viscosity 810cPs	not unmixed viscosity 780cPs
2	not unmixed viscosity 950cPs	not unmixed viscosity 900cPs	not unmixed viscosity 840cPs
3	not unmixed viscosity 890cPs	not unmixed viscosity 850cPs	not unmixed viscosity 800cPs
4(comp)	not unmixed	--	--
5(comp)	unmixed	--	--

Table 2

Examples	chemical stability in the time at room temperature		
	48 hours	8 weeks	24 weeks
1	99.7%	99.2%	98.1
2	99.5%	98.5%	97.2%
3	99.3%	98.9%	98.0%
4(comp)	71.0%	--	--
5(comp)	99.2%	--	--

[0039] From the data reported in the Tables it can be noticed that physically stable water-based systems (Example 4 comp) containing in suspension fine crystals of the PAP peracid have not the necessary chemical stability, decreasing in quality due to the active principle decay, with loss of peroxidic oxygen.

[0040] Viceversa it happens that chemically stable water-based systems (Example 5 comp) containing in suspension fine crystals of the PAP peracid, have not the necessary physical stability, with loss of uniformity and decomposition in differentiated phases also just after the preparation.

Claims

1. Water-based dispersions of the ϵ -phthalimido peroxyhexanoic acid comprising as stabilizers copolymers of methyl-vinyl-ether with the acid and/or maleic anhydride, in 1:1 ratio having an alternate structure.
2. Dispersions according to claim 1, wherein the weight average molecular weight of the copolymers is in the range 200,000-2,000,000.
3. Dispersions according to claims 1-2, wherein the amount of ϵ -phthalimido peroxyhexanoic acid ranges between 1-30% by weight, preferably between 3-20% by weight.
4. Dispersions according to claims 1-3, wherein the stabilizer amount ranges from 0.2-5% by weight, preferably

1.5-4% by weight, still more preferably 2-4% by weight.

- 5 5. Dispersions according to claims 1-4, wherein additional components such as polymers of natural origin of polysaccharide type are present.
6. Dispersions according to claim 5, wherein the polysaccharides are selected from guar rubber and xanthan rubber.
7. Dispersions according to claims 5-6, wherein the polysaccharides are in the range 0.1%-1.5% by weight.
- 10 8. Dispersions according to claims 1-7, wherein components having the function to stop the catalytic action of heavy metal ions on the decomposition of the peroxyacid are present, in an amount from 0.005 to 5% by weight, selected from chelants and/or sequestrants.
- 15 9. Dispersions according to claim 8, wherein said components are selected from one or more of the following: quinoline and its salts, alkaline metal polyphosphates, picolinic and dipicolinic acid, mono- or polyphosphonic acids, preferably the 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP).
10. Use of the dispersions according to claims 1-9 in detergent, or hygienizing, cosmetic applications.

Patentansprüche

- 25 1. Wäßrige Dispersionen der ε-Phthalimidoperoxyhexansäure, umfassend als Stabilisatoren Copolymere von Methylvinylether mit Maleinsäure und/oder Maleinsäureanhydrid in einem 1:1-Verhältnis mit einer alternierenden Struktur.
2. Dispersionen nach Anspruch 1, worin das gewichtsmittlere Molekulargewicht der Copolymere im Bereich von 200.000 bis 2.000.000 liegt.
- 30 3. Dispersionen nach den Ansprüchen 1 bis 2, worin die Menge an ε-Phthalimidoperoxyhexansäure zwischen 1 und 30 Gew.-%, vorzugsweise zwischen 3 und 20 Gew.-% beträgt.
4. Dispersionen nach den Ansprüchen 1 bis 3, worin die Stabilisatormenge von 0,2 bis 5 Gew.-%, vorzugsweise 1,5 bis 4 Gew.-%, noch mehr bevorzugt 2 bis 4 Gew.-% beträgt.
- 35 5. Dispersionen nach den Ansprüchen 1 bis 4, worin weitere Komponenten, wie Polymere natürlichen Ursprungs vom Polysaccharidtyp, zugegen sind.
6. Dispersionen nach Anspruch 5, worin die Polysaccharide unter Guargummi und Xanthangummi ausgewählt sind.
- 40 7. Dispersionen nach den Ansprüchen 5 bis 6, worin die Polysaccharide im Bereich von 0,1 bis 1,5 Gew.-% vorliegen.
8. Dispersionen nach den Ansprüchen 1 bis 7, worin Komponenten mit der Funktion, die katalytische Wirkung von Schwermetallionen auf die Zersetzung der Peroxysäure abzubrechen, in einer Menge von 0,005 bis 5 Gew.-%, ausgewählt unter Chelatisierungsmitteln und/oder Sequestrierungsmitteln, zugegen sind.
- 45 9. Dispersionen nach Anspruch 8, worin die Komponenten aus einer oder mehreren der nachstehenden Verbindungen ausgewählt sind: Chinolin und dessen Salze, Alkalimetallpolyphosphate, Picolinsäure und Dipicolinsäure, Monooder Polyphosphonsäuren, vorzugsweise die 1-Hydroxyethyliden-1,1-diphosphonsäure (HEDP).
- 50 10. Verwendung der Dispersionen nach den Ansprüchen 1 bis 9 in reinigenden oder hygienisierenden, kosmetischen Anwendungen.

Revendications

- 55 1. Dispersions aqueuses d'acide ε-phthalimido peroxyhexanoïque comprenant comme stabilisants des copolymères d'éther méthylvinyle avec l'acide et/ou l'anhydride maléique, dans un rapport 1:1, ayant une structure alternée.

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2. Dispersions selon la revendication 1, dans lesquelles la masse moléculaire moyenne en poids des copolymères est dans la gamme de 200 000 à 2 000 000.
3. Dispersions selon les revendications 1 à 2, dans lesquelles la quantité d'acide ϵ -phthalimido peroxyhexanoïque se situe entre 1 et 30% en poids, de préférence entre 3 et 20% en poids.
4. Dispersions selon les revendications 1 à 3, dans lesquelles la quantité de stabilisant se situe dans la plage de 0,2 à 5 % en poids, de préférence de 1,5 à 4% en poids, de préférence encore de 2 à 4% en poids.
5. Dispersions selon les revendications 1 à 4, dans lesquelles des composants supplémentaires tels que des polymères d'origine naturelle de type polysaccharide sont présents.
6. Dispersions selon la revendication 5, dans lesquelles les polysaccharides sont choisis parmi la gomme guar et la gomme xanthane.
7. Dispersions selon les revendications 5 à 6, dans lesquelles les polysaccharides sont dans la plage de 0,1% à 1,5% en poids.
8. Dispersions selon les revendications 1 à 7, dans lesquelles des composants, qui ont pour fonction d'arrêter l'action catalytique des ions métalliques lourds sur la décomposition du peroxyacide, sont présents, dans la proportion de 0,005 à 5% en poids, et choisis parmi des chélateurs et/ou des séquestrants.
9. Dispersions selon la revendication 8, dans lesquelles lesdits composants sont choisis parmi un ou plusieurs des composés suivants : la quinoline et ses sels, les polyphosphates de métaux alcalins, l'acide picolinique et dipicolinique, les acides mono- ou poly-phosphoniques, de préférence l'acide 1-hydroxyéthylidène-1,1-diphosphonique (HEDP).
10. Utilisation des dispersions selon les revendications 1 à 9 dans des détergents ou des applications d'hygiène, ou des applications cosmétiques.